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Sertifikaat

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Certificate

REPUBLIC OF SOUTH AFRICA

PATENT OFFICE
DEPARTMENT OF TRADE AND
INDUSTRY



the documents attached hereto are true copies of Forms P1, P2
and provisional specification and drawing of South African Patent Application
No. 2003/2868 in the name of Sasol Technology (Proprietary) Limited

Filed : 11 April 2003
Entitled : Processing of the
Product Streams from
a Fischer-Tropsch
Reaction

PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

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PRETORIA

in die Republiek van Suid-Afrika, hierdie
in the Republic of South Africa, this

3rd dag van June 2004
day of

Registrar of Patents

REPUBLIC OF SOUTH AFRICA		REGISTER OF PATENTS			PATENTS ACT, 1978	
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FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)						
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APPLICANTS SUBSTITUTED:						DATE REGISTERED
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ASSIGNEE(S)						
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54	PROCESSING OF THE PRODUCT STREAMS FROM A FISCHER-TROPSCH REACTION					
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APPLICATION FOR A PATENT
AND ACKNOWLEDGEMENT OF RECEIPT 11.04.03
(Section 30 (1) – Regulation 22)

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REVENUE

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The granting of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

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TAKOMSTE
REPUBLIC VAN SUID AFRIKA
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21

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FULL NAME(S) OF APPLICANT(S)

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TITLE OF INVENTION

54

PROCESSING OF THE PRODUCT STREAMS FROM A FISCHER-TROPSCH REACTION

THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. THE EARLIEST PRIORITY CLAIM IS:

COUNTRY: NIL

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THIS APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO.

21 01

THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND IS BASED ON APPLICATION NO.

21 01

THIS APPLICATION IS ACCCOMPANIED BY:

- 1. A single copy of a provisional specification of 10 pages.
- 2. Drawings of 2 sheets.
- 3. Publication particulars and abstract (Form P.8 in duplicate).
- 4. A copy of Figure of the drawings (if any) for the abstract.
- 5. Assignment of invention.
- 6. Certified priority document.
- 7. Translation of the priority document.
- 8. Assignment of priority rights.
- 9. A copy of the Form P.2 and the specification of S.A. Patent Application No .
- 10. Declaration and power of attorney on Form P.3.
- 11. Request for ante-dating on Form P.4.
- 12. Request for classification on Form P.9.
- 13. Form P.2 in duplicate.
- 14. Other.

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Dated: 11 April 2003

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REGISTRAR OF PATENTS, TRADE MARKS AND COPYRIGHT
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REGISTRATEUR VAN PATENTE, MODELLÉ, HANDELSNAAM EN UUITEURSREGISTRAAT
REGISTRAR OF PATENTS

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PROVISIONAL SPECIFICATION

(Section 30(1) – Regulation 27)

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TITLE OF INVENTION

54	PROCESSING OF THE PRODUCT STREAMS FROM A FISCHER-TROPSCH REACTION
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PROCESSING OF THE PRODUCT STREAMS FROM A FISCHER-TROPSCH REACTION

BACKGROUND OF THE INVENTION

THIS invention relates to a method of producing three hydrocarbon fractions from Fischer-Tropsch synthesis reaction product, typically a low temperature Fischer-Tropsch reaction. One of the hydrocarbon fractions that is produced is particularly suitable for linear alkyl benzene production.

Alkyl benzene derivatives, such as alkyl benzene sulphonates, are among others, used in detergent and surfactant product applications. Environmental legislation requires that these products are biodegradable. It is well known that, to be bio-degradable, it is important for the alkyl chain to be linear, i.e. with very little or no branching and low, if any, quaternary carbons.

In conventional processes for producing linear alkyl benzenes, a hydrocarbon stream is hydrogenated in order to convert oxygenates and olefin species in the stream to paraffins. Hydrogenation also allows for the removal of sulphur and nitrogen contaminants that may be present. Following the hydrogenation reaction, the resulting paraffin stream is fractionated into various carbon ranges. A carbon range, for example the C₈ to C₁₆ range, which includes branched paraffins, is passed through a molecular sieve. The branched paraffins are rejected as a raffinate stream, whilst the linear paraffins are passed through a dehydrogenation reactor to form an olefin/paraffin mixture. This mixture is then fed to an alkylation plant and reacted with benzene to form linear alkyl benzene (LAB). The linear alkyl benzene is then sulphonated to form linear alkyl benzene sulphonates (LAS). A problem with this approach is the relatively high cost of paraffinic starting material and the high cost associated with the production of linear paraffins from kerosene feedstocks.

2003/2868

In the Fischer-Tropsch process, synthesis gas (carbon monoxide and hydrogen), obtained from gasification of coal or reforming of natural gas, is reacted over a Fischer-Tropsch catalyst to produce a mixture of hydrocarbons ranging from methane to waxes and smaller amounts of oxygenates.

In a low temperature Fischer-Tropsch reaction, the reaction takes place in a slurry bed reactor or fixed bed reactor, preferably a slurry bed reactor, at a temperature in the range of 160°C - 280°C and a pressure in the range of 18-50 bar, in the presence of a catalyst. The catalyst may include iron, cobalt, nickel or ruthenium. However, a cobalt-based catalyst is preferred for the low temperature reaction. Usually, the cobalt catalyst is supported on an alumina support.

During the Fischer-Tropsch reaction, a lighter hydrocarbon vapour phase is separated from a liquid phase comprising heavier liquid hydrocarbon products. The heavier liquid hydrocarbon product (waxy products) is the major product of the reaction. Whilst the product slate produced by Fischer-Tropsch reactions using different catalysts and operating conditions will be different, in all cases the product slate contains some waxy, highly paraffinic material which needs to be upgraded into usable, final products, such as middle distillates, naphtha, solvents, lube oil bases, etc.

The lighter hydrocarbon vapour phase (which comprises gaseous hydrocarbon products, unreacted synthesis gas and water) is condensed to provide a "condensation product" which comprises an aqueous phase and a hydrocarbon condensation product phase.

United Kingdom Patent No. 669,313 in the name of California Research Corporation, United States Patent No. 3,674,885 in the name of Atlantic Richfield Company and International Patent Publication No. WO 01/64610 in the name of Chevron USA Inc. disclose the use of a hydrocarbon condensate from the Fischer-Tropsch process, in the production of alkyl

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benzene. These references disclose that the hydrocarbon condensate contains olefins which are used in the alkylation reaction to form linear alkyl benzene. These references are limited to the use of "high temperature" Fischer-Tropsch processes wherein the Fischer-Tropsch reaction is carried out temperatures of approximately 300°C and higher, and the preferred catalysts are iron-containing catalysts, for the production of the hydrocarbon condensate. The high temperature Fischer-Tropsch processes were found to be suitable because the hydrocarbon condensate contains a high concentration of olefins, usually in the region of around 70%. Although these references refer to linear olefins, those skilled in the art know that in practice the olefins obtained from a high temperature Fischer Tropsch process exhibit more than 10 % branching.

SUMMARY OF THE INVENTION

According to the invention there is provided a method of producing three hydrocarbon fractions from a hydrocarbon condensate and a wax fraction product stream from a Fischer-Tropsch reaction, the hydrocarbon fractions being:

- 1) hydrocarbon fraction A, being a hydrocarbon fraction having a boiling point above 25°C and an end point below 200°C;
 - 2) hydrocarbon fraction B including at least a mixture of alkanes, alkenes and oxygenates having a boiling point in the range 100-300°C; and
 - 3) hydrocarbon fraction C having a boiling point in the range 120-400°C;
- the method including the steps of:
- a) fractionating the hydrocarbon condensate stream, or a derivative thereof, from the Fischer-Tropsch reaction to form at least three fractionated hydrocarbon condensate streams wherein at least one of the three fractionated hydrocarbon condensate streams is hydrocarbon fraction B;
 - b) hydroconverting at least the wax fraction product stream, or a derivative thereof, from the Fischer-Tropsch reaction;

- c) fractionating the hydroconverted wax product from step b) to obtain at least a hydroconverted light hydrocarbon stream and a hydroconverted distillate stream; and
- d) selectively blending the products of steps a) and c) to obtain hydrocarbon fractions A and C; and
- e) transferring the hydrocarbon condensate stream from step (a) that constitutes hydrocarbon fraction B to a process for the production of linear alkyl benzenes.

The method may include the additional step of transferring a waxy unconverted fraction from step b) to a process for the production of high viscosity index base oils by either solvent extraction or catalytic isodewaxing.

Typically, the Fischer-Tropsch reaction is a low temperature Fischer-Tropsch reaction carried out in a slurry bed reactor at a temperature of 160°C - 280°C, preferably 210°C - 260°C, and in the presence of a cobalt catalyst to provide a hydrocarbon condensate containing 60 to 80% by weight paraffins and 10 to 30% by weight, typically less than 25% by weight, olefins.

Typically, the hydrocarbon fraction A has a boiling point above 30°C and an end point below 175°C, preferably below 160°C.

Typically, the hydrocarbon fraction B has a boiling point in the range is 145 - 255°C , and preferably the temperature range is 165-240°C.

Typically, the hydrocarbon fraction C has a boiling point in the range 150-380°C, more typically 160 -360°C.

The process for the production of linear alkyl benzenes referred to in step e) may comprise alkylation and catalytic dehydrogenation.

22003/2068

According to a further aspect of the invention there is provided a method of producing an additional hydrocarbon fraction being hydrocarbon fraction D including medium to high molecular mass alkanes, both linear and isomerised, having a boiling point typically above 380°C, more typically above 400°C.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a block diagram of a process according to the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

This invention relates to a method of producing or working-up three predetermined hydrocarbon fractions from the product streams from a Fischer-Tropsch reaction. These three hydrocarbon fractions include:

- 1) a hydrocarbon fraction A having a boiling point above the 25°C and more typically above 30°C, and an end point below 200°C, preferentially below 175°C and even more preferentially below 160°C,
- 2) a hydrocarbon fraction B including a mixture of 60% to 80% by weight alkanes, 15-30% by weight alkenes and 5% to 10% by weight oxygenates boiling preferentially in the 100-300°C, and more preferentially in the range 165-240°C and where the overall linearity of the mixture is greater than 92%, preferentially greater than 95%, and
- 3) a hydrocarbon fraction C being a hydrocarbon fraction boiling in the range 120-400°C, more typically in the 150-380°C and preferably in the range 240-360°C.

The invention also extends to producing or working-up a fourth hydrocarbon fraction D including medium to high molecular mass alkanes, both linear and isomerised, boiling typically above 380°C and preferably above 400°C.

The process as proposed includes several advantages over conventional processes used in the so-called gas-to-liquids (GTL) schemes. These advantages include:

- 1) improvement in the density and heat content of hydrocarbon fraction C;
- 2) production of an improved synthetic feedstock for producing linear alkyl benzenes, namely hydrocarbon fraction B; Fraction B is particularly suitable to the production of LAB, due to the fact that the fraction contains the required high degree of linearity and while relatively low olefin content in the C₁₀ to C₁₃ hydrocarbon range it is surprisingly found that it can be utilized economically/advantageously,
- 3) production of a high viscosity index (HVI) base oil feedstock – hydrocarbon fraction D. This product can also lead to the recovery of a hydrogenated wax comprising both normal and isomerised alkanes; and
- 4) production of a high performance feedstock suitable for the production of lower olefins, as described in technical literature (*Performance of the Sasol SPD Naphtha as Steam Cracking Feedstock*, American Chemical Society – Paper 561940, presented at National Meeting, Boston, August 2002)

The production or work up method which forms the subject matter of this invention is based on the processing of the two product streams derived from a Fischer-Tropsch reaction, namely a wax fraction product stream and a hydrocarbon condensate:

- The wax fraction product stream typically has a true boiling point (TBP) in the range of about 70°C to 700°C, more typically in the range 80°C to 650°C.
- The hydrocarbon condensate typically has a true boiling point (TBP) in the range -70°C to 350°C, more typically -10°C to 340°C, usually -70°C to 350°C.

A typical composition of the wax fraction product stream and the hydrocarbon condensate is set out in Table 1.

Table 1
(vol % distilled)

Distillation Range	Hydrocarbon Condensate	Wax Fraction Product Stream
■ C5-160°C	44	3
■ 160-270°C	43	4
■ 270-370°C	13	25
■ 370-500°C	NR	40
■ >500°C	NR	28
Total	100	100

The hydrocarbon condensate includes olefins and paraffins in the C₄ to C₂₆ range, and oxygenates including alcohols, esters, aldehydes, ketones, acetals and acids.

As is described in the section of this document entitled "Background of the Invention", in the Fischer-Tropsch process, synthesis gas (carbon monoxide and hydrogen), obtained from gasification of coal or reforming of natural gas, is reacted over a Fischer-Tropsch catalyst to produce a mixture of hydrocarbons ranging from methane to waxes and smaller amounts of oxygenates. The synthesis gas is typically in the range of molar ratios 3:1 to 1:1 (hydrogen to carbon monoxide).

In a low temperature Fischer-Tropsch reaction, the reaction takes place in a slurry bed reactor or fixed bed reactor, preferably a slurry bed reactor, at a temperature in the range of 160°C - 280°C, preferably 210°C - 260°C, and a pressure in the range of 18-50 bar, preferably between 20-30 bar, in the presence of a catalyst. The catalyst may include iron, cobalt, nickel or ruthenium. However, a cobalt-based catalyst is preferred for the low temperature reaction. Usually, the cobalt catalyst is supported on an alumina support.

During the Fischer-Tropsch reaction, a lighter hydrocarbon vapour phase is separated from a liquid phase comprising heavier liquid hydrocarbon products. The heavier liquid hydrocarbon product (waxy products) is the major product of the reaction and may, for example, be hydrocracked to produce diesel and naphtha. While the product slate produced by different Fischer-Tropsch reactions using different catalysts and operating conditions will be different, in all cases the product slate contains some waxy, highly paraffinic material which need to be upgraded into usable products.

The lighter hydrocarbon vapour phase which comprises gaseous hydrocarbon products, unreacted synthesis gas and water is condensed to provide a hydrocarbon condensate which comprises an aqueous phase and a hydrocarbon condensation product phase.

An embodiment of the invention is exemplified with reference to Figure 1. In this embodiment two liquid hydrocarbon products are separated from the conversion of synthesis gas (syngas) by the Fischer-Tropsch reaction in the Fischer-Tropsch reaction unit 10.

The hydrocarbon condensate is collected as stream 11 and transferred to an atmospheric distillation unit (ADU) 20 where it is separated into three streams. The lighter stream 13 is transferred to a hydrotreater 40 for complete saturation and removal of heteroatoms. (This step is optional to the process.) The resulting product is collected as stream 17. A middle stream 14 is collected as a second product and transferred to linear alkyl benzene processing operation. A heavier hydrocarbon fraction is collected as stream 15 and transferred to the hydroconversion unit 30.

The wax fraction product stream 12 from the Fischer-Tropsch reaction unit 10, is blended with stream 15 from the ADU before being sent as stream 16 to a hydroconversion unit 30. Here at least three products are produced as well as a mixture of light hydrocarbons (not shown in the figure) as a gaseous stream. A light hydrocarbon product stream 18 and a heavier

2003/2009

hydrocarbon product stream 31 is sent to storage. There is a fourth stream that is produced – also not shown in the figure – that includes all heavy unconverted hydrocarbon species. This is usually recycled to extinction within the hydroconversion unit 30. As an alternative to the process, a heavy hydroconverted stream can be recovered as stream 27 and made available for the preparation of high visibility index (HVI) base oils by either solvent extraction or catalytic dewaxing. These two processing options are well known in the art and are not described in detail here. Should solvent extraction be used, it is possible to obtain as a by-product a highly paraffinic hydrogenated wax.

Stream 14, the middle stream from the ADU, which contains synthetic olefinic feedstock is sent to linear alkyl benzene processing starting with unit 50. Unit 50 is an oxygenates removal unit operation. In the prior art, many methods of extracting oxygenates from hydrocarbon streams are suggested. Such removal methods include hydrogenation, azeotropic distillation, extractive distillation, vapour phase dehydration, liquid phase dehydration and liquid-liquid extraction. It has been found that distillation, liquid-liquid extraction and dehydration processes are preferred as they preserve the olefin concentration, which is a desired result. Two streams are obtained from the oxygenate removal unit 50: an oxygenates rich stream 22 sent to storage, and a stream 21 comprising mostly paraffins and olefins is sent to the alkylation unit 60 where it is alkylated with benzene 23 transferred from storage. The products from the alkylation unit 60 are separated into two streams: the linear alkyl benzene product 26 and an unconverted stream 24. The latter 24, comprising alkanes, is sent to the dehydrogenation unit 70 to undergo catalytic dehydrogenation. Once processed, this is returned via stream 25 to the alkylation unit 60.

The two light liquid hydrocarbon streams, hydrotreated product 17 and hydroconverted product 18 are blended and sent to storage as a highly paraffinic single stream 19.

Process conditions for hydrotreating and hydroconversion of streams from a Fischer-Tropsch reaction unit can be varied to achieve a wide range of product compositions. The process conditions are usually laboriously chosen after extensive experimentation to optimise yields, process performance and catalyst life. Table 2 gives a list of one such set of typical conditions.

Table 2 – Process Conditions for Hydroprocessing of the Fischer-Tropsch Streams

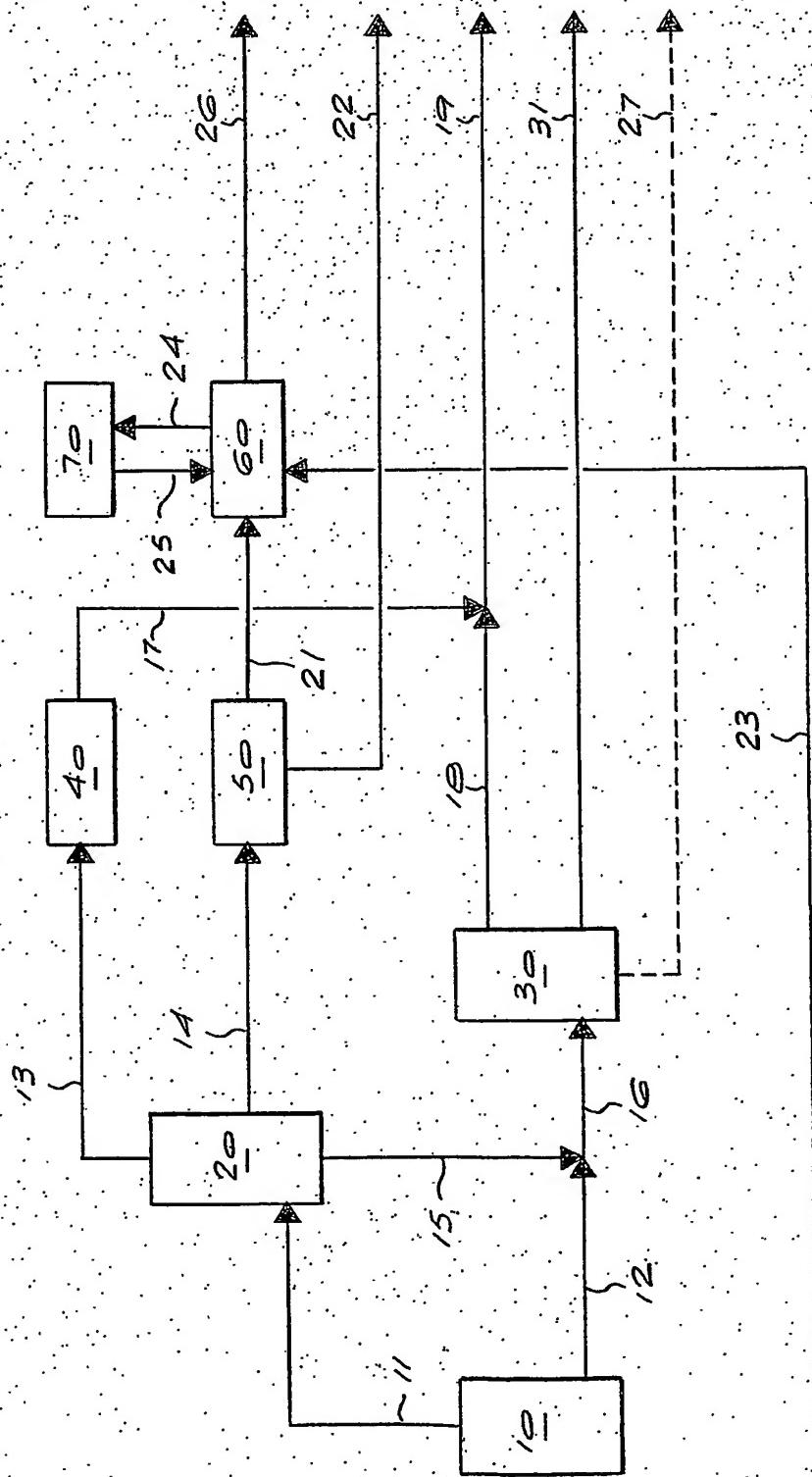
Set of Conditions	Hydrotreating Range		Hydroconversion Range	
	Broad	Preferred	Broad	Preferred
Temperature, °C	150-450	250-350	150-450	340-400
Pressure, bar-g	10-200	30-80	10-200	30-80
H ₂ rate, m ³ n/m ³ feed	100-2000	800-1600	100-2000	800-1600
Conversion (note 1)	NA	NA	30 – 80	50 – 70

- Note 1 Expressed as material boiling above 370°C that disappears during the process (mass %)

Dated this 11th day of April 2003

Spoor & Fisher
Applicants Patent Attorneys

11



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